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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES  
FOR

ADVANCED MATERIALS RESEARCH PROGRAM

Fourth Quarterly Progress Report

covering the period  
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I. SUMMARY

The period covered by this report has been devoted to a series of impurity analyses on MgO and TaC materials. The materials have been both powders and compacts. Metallic as well as gaseous impurities have been determined.

A portion of this period has been used to attempt to correlate hydrogen content as measured by hot extraction with OH content measured mass spectrographically. This is a difficult problem, due in part to the nature of the material, and also the common occurrence of water vapor as a residual gas in the vacuum system of the spectrograph.

As a further check on mass-spectrographic analyses, a series of wet and colorimetric chemical methods are being investigated. The elements, sodium, potassium, calcium, fluorine, and silicon, are being determined by these methods because emission-spectrographic analyses are somewhat doubtful in these cases.

Details of these investigations are given in the following sections.

II. ACTIVITY DURING THE REPORTING PERIOD

A. MgO Analyses.

A series of seven MgO samples selected from various points in the JPL process for preparation of pure MgO from magnesium metal has been analyzed mass spectrographically. These materials were either powders or compacts.

The powdered materials were mixed with pure silver powder (two parts by weight silver to one part by weight MgO), pressed into appropriate shape, and run in the mass spectrograph. This has proven to be a reliable and accurate procedure. The major problems with this type of analysis are poor mixing, which results in an inhomogeneous electrode, and contamination from the die. We have been able to avoid both of these problems by using an extended mixing time and extensive removal of the surface of the electrode prior to analysis.

The compacted samples have been analyzed by a new technique which circumvents the use of a conducting additive. This method involves direct sparking of two MgO electrodes at high (50-60 kV) spark voltages. The advantages of the method are obvious: there is no contamination from crushing or handling the sample; and the sensitivity and accuracy are at least as good as those of the silver powder method. A typical mass spectrum of an MgO material is shown in Fig. 1.

One disadvantage is the enhancement of thermal ionization. During the sparking of two MgO electrodes, enough heat is generated to cause the electrodes to glow. This is more than enough heat to ionize elements such as sodium and potassium, and would lead to erroneously high results. However, the use of the doubly ionized line,  $\text{Na}^{++}$  or  $\text{K}^{++}$ , at masses 11.5 and 19.5, will give a true indication of the concentration of the element. The results of these analyses are shown in Table 1, on the following page.

Emission-spectrographic analyses as a check on the mass spectrograph have also been performed for those elements which can be handled by emission techniques. The emission method involves the use of a series of carefully prepared standards which are of known impurity content. The spectrum of

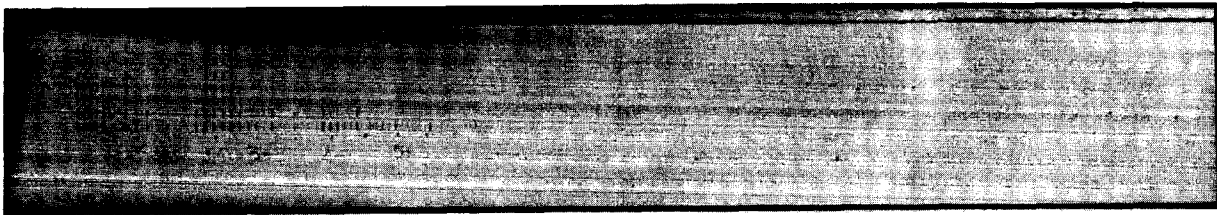


FIG. 1 Mass spectrum produced from two MgO electrodes. Spark voltage 5.5 kV. The high aluminum content is from aluminum holders.

the unknown is compared to these standards and this has resulted in reasonable comparisons between mass and emission values. Table 2 lists the results of emission-spectrographic analyses.

Table 1. Mass-spectrographic analyses of JPL MgO (ppma).

Sample No:	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>10</u>	<u>11</u>	<u>13</u>
Boron	3	1	5	5	3	8	< 1
Nitrogen	195	240	170	95	110	210	200
Fluorine	17	200+	125	250+	250+	30	50
Aluminum	-	-	-	30	15	5	30
Sodium	< 1	1	1	< 1	< 1	< 1	< 1
Silicon	190	175	115	170	75	65	80
Calcium	12	75	60	30	40	30	30
Chlorine	65	125	110	95	45	35	55
Iron	8	3	20	8	20	14	10

Table 2. Emission-spectrographic analyses of JPL MgO (ppma).

Sample No.	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>10</u>	<u>11</u>	<u>13</u>
Boron	1	1	1	1	1	3	1
Aluminum	3	7	15	30	20	5	5
Silicon	30	10	20	7	15	30	30
Calcium	5	10	15	5	10	25	15
Iron	2	2	2	2	2	7	5

The most obvious piece of information to be derived from these analyses concerns the TTA extraction of the magnesium nitrate solution. The high purity of the magnesium starting material and the lesser purity of the samples numbered 3, 4, 5, and 10, indicate that the TTA extraction is not only harmful, but unnecessary. Contamination of high purity materials with reagents is not unusual and this is apparently the case with the extraction step.

The determination of H and OH in these samples is proving to be a difficult problem. The presence of water vapor as one of the residual gases in the vacuum system is the most likely cause of this trouble.

A series of four samples of known OH content (OP 125, OP 128, OP 111, OP 14) has been analyzed mass spectrographically in an attempt to use the OH peak at mass 17 as an indication of the hydrogen content. These experiments have been unsuccessful. The peak at mass 17 changes over a factor of thirty, even on successive runs on the same sample. Continual baking of the source seems to have no effect on the peak. It is becoming apparent that we have a water adsorption problem which may best be solved with the aid of a liquid nitrogen cooled trap inside the source. This type of trap has been reported in the literature to lead to greater reproducibility for the analysis of volatiles.

As an indication of the variability we have been seeing, Table 3 shows the relative heights of the mass 17 peak during five successive runs on the same sample. The sample was baked between runs and the source pressure was  $5 \times 10^{-8}$  torr.

Table 3. Relative height of mass 17 peak for OP 128.

<u>Plate No.</u>	<u>PPM (atomic)</u>
404	1000
405	50
406	300
407	50
408	100

We plan to install a source cold trap in the near future and re-run these samples.

The determination of hydrogen by hot extraction has not proved to be as accurate as this technique can be for metallic systems. The four samples, OP 125, OP 128, OP 111, and OP 14, have been run using hot extraction, but once again there has been a large variation in successive runs. The reproducibility of hot extraction for hydrogen in metals is  $\pm 20\%$  at worst. We have found variations much larger than this for repeat runs on the same sample. A relative ranking of the four samples has been made and is as follows: OP 125 > OP 128 > OP 14 = OP 111. Further work will be done here.

The use of the mass spectrograph for hydrogen analyses is now being investigated. Our first checks of the instrument blank level for hydrogen indicated extremely high values (600 ppma). Some recent work at Sandia Corporation, however, indicated that it has been possible to analyze hydrogen at much lower levels — in fact, as low as 1-10 ppm atomic. We have made another check on our instrument with materials used in the Sandia investigation and find that it may be possible for us to do hydrogen at these low levels. A standard molybdenum alloy containing 1.0 ppm (weight) hydrogen has been analyzed with excellent results (1.8 ppm weight by our instrument). We plan to investigate this technique.

A paper describing our technique for the mass-spectrographic determination of interstitial elements has been written, approved by JPL, and will be submitted to Analytical Chemistry.

B. Analysis of Tantalum Carbide.

A series of eight tantalum carbide specimens is being analyzed for oxygen using the mass spectrograph. Since the materials are powders they are being mixed with pure silver prior to analysis. Results on the

first five samples are available. The values are listed in Table 4.

Table 4. Oxygen content of CIBA TaC.

<u>Sample No.</u>	<u>Oxygen (wt. %)</u>
3 - 2	.060
3 - 1	.053
2 - 5	.060
2 - 3	.028
2 - 2	.022

These values do not agree with vendor analyses, but we will wait until the last three samples are done before attempting any analysis of the data.

C. Wet Methods for Selected Impurities.

As a further check on the accuracy of the mass spectrograph, we are currently using wet chemical methods to determine the concentration of such elements as sodium, potassium, calcium, fluorine, and silicon. Sodium, potassium, and calcium will be analyzed by flame photometric techniques. The sensitivity of this method is more than adequate for the levels of these elements in MgO and the accuracy is also good. This equipment will be available at the Research Center early next year.

Fluorine will be analyzed by a polarographic procedure. The sensitivity and accuracy of the method are adequate. Silicon will be analyzed colorimetrically by the molybdate method.

D. Laser Source.

We have made two trips in the past month to laboratories which have experience with laser sources in the mass spectrograph (RCA and G.E.). Both laboratories feel that there is need for improvement before the laser



becomes a useful tool for the location of impurities. Another useful method has been noted for this type of analysis. The use of a finely pointed electrode as a probe has found some application for impurity location. This work has been done at General Telephone Laboratories and shows part-per-million sensitivity in areas less than 10 mils square.

The most common problem with the laser source has been variation in the amount of ion current produced. Successive laser pulses in the same spot produce ion currents which vary by a factor of one hundred.

### III. PLANS FOR NEXT QUARTER

During the next quarter we shall attempt to develop a suitable method for hydrogen and hydroxide. The mass spectrograph would be the easiest tool if reasonable correlations can be made.

Wet analyses of fluorine and silicon in JPL MgO materials will be performed by methods outlined in Sec. II. We will also attempt to correlate tantalum-carbon ratios with oxygen content in tantalum carbide specimens.

### IV. OTHER ACTIVITIES

We have participated in a round-robin for the analysis of interstitials in refractory metals sponsored by the National Academy of Science. Most of the laboratories used standard methods, but our values were in good agreement as shown.

		<u>M.S.</u>	<u>True Value ppm wt.</u>
Molybdenum	Carbon	215	230
	Nitrogen	7	16
	Oxygen	33	7
Tantalum			
	Carbon	20	17
	Nitrogen	7	18
	Oxygen	16	14
Tungsten			
	Carbon	27	9
	Nitrogen	11	6
	Oxygen	6	7
Niobium			
	Carbon	28	10
	Nitrogen	12	43
	Oxygen	34	68